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THE ADSORPTION OF WATER, ETHYL ALCOHOL, ETHYL ACETATE, AND ACETIC ACID VAPORS BY TUNGSTIC AND ZIRCONIUM OXIDES; ITS BEARING ON HETEROGENEOUS CATALYSES

BY

MURRAY JOHN RICE

B.S. Kalamazoo College, 1919

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DISSERTATION IN CHEMISTRY

Submitted in Partial Fulfillment of the Requirements for the

DEGREE OF

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IN

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ACKNOWLEDGMENT

The author wishes to make acknowledgment to Professor J. N. Pearce, under whose direction this work has been carried out.

THE ADSORPTION OF WATER, ETHYL ALCOHOL, ETHYL ACETATE AND ACETIC ACID VAPORS BY TUNGSTIC AND ZIRCONIUM OXIDES; ITS BEARING ON HETEROGENEOUS CATALYSIS

J. N. PEARCE AND M. J. RICE

It has long been known that many oxides act catalytically as dehydrating and dehydrogenating agents. The dehydration of alcohol vapor during its passage through an earthen tube heated to redness was observed by Priestley[1] as long ago as 1783. At a slightly later date Deimann[2] found that alcohol vapor passed over heated alumina and silica is decomposed to ethylene and water and a small amount of hydrogen. Under certain conditions ethyl ether[3] is also formed. Baskerville[4] failed to obtain ethyl ether with thoria at temperatures even as low as 250°, but he did find that the simultaneous dehydration of a phenol and an alcohol by thoria at 400° gives a mixed aliphatic ether.

Sabatier and Mailhe[5] conducted an extended series of experiments using various metallic oxides and several vapors, and observed that in many cases there is a dehydrogenation as well as dehydration. They report thoria to be more active than alumina and state that it behaves exclusively as a dehydrating agent. While alumina is an exceedingly strong dehydrating agent it also possesses some dehydrogenating power. Kramer and Reid,[6] however have shown that under certain conditions thoria may also act as a dehydrogenating agent toward alcohols. They also state that overheating in preparation seems to lessen the activity of the thoria.

Sabatier and Mailhe[5] have found that the specific catalytic action of the oxide is dependent on the temperature of the reaction, since alcohols are converted into ethylenic hydrocarbons by ThO_2, Al_2O_3, and W_2O_3 between 300° and 350°, while ethers are produced at temperatures below 250°. They consider that the mechanism of the process involves the formation of a complex intermediate compound, $ThO(OC_nH_{2n} + 1)_2$. This may either break up to give ethylene and water, or, under other conditions, it may react with another molecule of alcohol to give an ether, regenerating the metallic oxide. Engelder[7] has shown that the presence of water vapor or of hydrogen in the incoming alcohol vapor also determines the ratio of ethylene and hydrogen

[1] Priestley: Phil. Trans., **73**, 429 (1783).

[2] Deimann: Crell's Ann., **2**, 312, 430 (1795).

[3] Grigorieff: J. Russ. Phys. Chem. Soc., **33**, 173 (1901).

[4] Baskerville: J. Am. Chem. Soc., **35**, 93 (1913).

[5] Sabatier and Mailhe: Compt. rend., **136**, 738, 921, 983 (1903); **146**, 1376 (1908); **148**, 1734 (1909); **150**, 823 (1910); **152**, 358, 494 (1911).

[6] Kramer and Reid: J. Am. Chem. Soc., **43**, 880 (1921).

[7] Engelder: J. Phys. Chem., **21**, 676 (1917).

in the resulting decomposition products. Senderens[8] obtained ethers by passing the vapors of methyl and ethyl alcohols over alumina at temperatures between 240° and 260°, and he represents the reaction as merely one of dehydration. The higher alcohols, however, give either a low yield of ether, or none at all, ethylenic hydrocarbons being the chief products. With W_2O_3 only small amounts of methyl and ethyl ethers are formed and no ether is obtained with ThO_2. By heating acids and esters in the presence of these oxides he has also obtained ketones. He represents the reaction in this case as a dehydration followed by a decomposition; the acid anhydride is first formed and this then breaks up to give the ketone and CO_2. This idea was confirmed by the fact that CO_2 and dimethyl ketone are obtained when acetic anhydride vapor is passed over Al_2O_3 at 300°. In another paper Senderens[9] has shown that both aliphatic and aromatic acids yield ketones when heated in the presence of ThO_2, ZrO_2 and UO_2.

The effect of Al_2O_3, ThO_2 and TiO_2 on ethyl acetate in the neighborhood of 400° is summarized by Sabatier[10] in the following manner:

$$2\ CH_3COOC_2H_5\ (Al_2O_3) = (CH_3)_2CO + 2\ C_2H_4 + CO_2 + H_2O,$$
$$2\ CH_3COOC_2H_5\ (ThO_2) = (CH_3)_2CO + C_2H_4 + CO_2 + C_2H_5OH, \text{ and}$$
$$CH_3COOC_2H_5\ (TiO_2) = CH_3COOH + C_2H_4.$$

An extended investigation of the activity of oxide catalysts at temperatures between 300° and 400° by Sabatier and Mailhe[11] shows that a majority of oxides promote two reactions simultaneously, one the process of dehydration, the other the process of dehydrogenation. The analysis of the gaseous products obtained in passing the vapor of ethyl alcohol over various oxides at 340° to 350° showed that with certain oxide catalysts ethylene only is produced. In general, however, the effluent gas is a mixture of ethylene and hydrogen in varying proportions depending on the catalyst employed. They have tabulated the different metallic oxides in the order of decreasing power of dehydrating alcohol, thus:

Oxide	$\%C_2H_4$	$\%H_2$	Oxide	$\%C_2H_4$	$\%H_2$
ThO_2	100.00	Trace	U_3O_8	24.0	76.00
Al_2O_3	98.50	1.5	Mo_2O_3	23.0	77.0
W_2O_3	98.5	1.5	Fe_2O_3	14.0	86.0
Cr_2O_3	91.0	9.0	V_2O_3	9.0	91.0
SiO_2	84.0	16.0	ZnO	5.0	95.0
TiO_2	63.0	37.0	MnO	0.0	100.0
BeO	45.0	55.0	SnO	0.0	100.0
ZrO_2	45.0	55.0	CdO	0.0	100.0

[8] Senderens: Bull., (4), **5**, 480 (1909); Compt. rend., **140**, 995 (1905); **148**, 227, 927 (1909); **150**, 111 (1910); Ann. Chim. Phys., (8) **28**, 243, 322 (1918).

[9] Senderens: Compt. rend., **150**, 702 (1910).

[10] Sabatier: "La Catalyse en Chimie organique," p. 341 (1920).

[11] Sabatier and Mailhe: Ann. Chim. Phys., (8), **20**, 341 (1910).

These data show that ThO_2 behaves almost exclusively as a dehydrating catalyst under the given conditions; its power as a dehydrogenating agent is practically nil. Alumina and tungstic oxides are only slightly less active dehydrating agents. The oxides of tin, manganese and cadmium are exclusively dehydrogenating catalysts, their dehydrating power is entirely suppressed. Between the two extremes the dehydrating and dehydrogenating powers of the metallic oxides vary rapidly. In general, the greater the dehydrating activity of a metallic oxide, the smaller is its dehydrogenating activity toward alcohol.

Adkins and Krause[12] state that the reaction induced by an oxide catalyst is influenced by the method of preparation and is not dependent merely on the metallic element present. They disagree with the intermediate compound theory of Sabatier and Mailhe.[5] In a later paper[13] Adkins suggests that the efficiency of the oxide depends on the character of the surface presented to the vapors, and in so doing he apparently accepts the view presented by Briggs.[14] The latter considers that the activation of charcoal for the adsorption of gases is dependent upon interstices of molecular dimensions formed by the elimination of carbon atoms from the carbon molecule or space lattice. The larger, microscopically visible pores or capillaries have apparently little to do with adsorption. Starting with this idea, Adkins[13] has advanced an hypothesis which considers that the catalytic activity of alumina is conditioned by its molecular porosity, or the distance between the aluminum atoms, and that this part is determined by the size, shape and position of the radicals attached to the aluminum atom when the aluminum compound passes into the solid state of the catalyst. To this end he prepared aluminum oxide by heating aluminum hydroxide and aluminum ethylate. Since the size of the molecules eliminated in the latter case is larger, the porosity should be greater. In turn, the adsorption capacity of the oxide formed from the aluminum ethylate should be correspondingly greater. All of the experimental evidence obtained by Adkins with aluminum catalysts, prepared in various ways, was found to be in complete harmony with this hypothesis. He was able to activate alumina preferentially, either for dehydration or for decarboxylation, by modifying the mode of preparation. In terms of his hypothesis he states that decarboxylation is favored by large molecular pores in alumina and that ethylene formation is favored by small pores.

This idea is also supported by Pease and Yung.[15] They find that alumina dehydrates alcohol at 300° to 400° to give pure ethylene, while ether is produced if the reaction is carried out at 240° to 250°. They also state that the size of the pores determines whether ethylene or ether is produced, large pores favoring the formation of ether, small pores favoring ethylene formation.

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[12] Adkins and Krause: J. Am. Chem. Soc., **44**, 385 (1922).
[13] Adkins: J. Am. Chem. Soc., **44**, 2175 (1922).
[14] Briggs: Proc. Roy. Soc., **100A**, 88 (1921).
[15] Pease and Yung: J. Am. Chem. Soc., **46**, 390 (1924).

However, since water is eliminated in either case, this cannot be a wholly satisfactory view.

In discussing the mechanism of catalysis by alumina, Boswell and Bayley,[16] and Boswell and Dilworth[17] have suggested the presence of a stable film of dissociated water in the form of charged H^+ and OH^-. They claim that the great stability of this film is indicated by the fact that it still persists after heating for 20 hours at 500° followed by two days heating over a Meeker burner. Further, that the stability of this film indicates that the H^+ and OH^- are arranged in alternate rows and completely envelope each oxide particle. Upon studying the reaction between C_2H_5OH and Al_2O_3 these authors conclude that the reaction is most satisfactorily represented thus:

$$\begin{matrix} H^+ \\ OH^- \\ Al_2O_3 \cdot H^+ \\ OH^- \end{matrix} + \begin{matrix} HCH_2 \\ HOCH_2 \end{matrix} = \begin{matrix} H^+ \\ OH^- \\ Al_2O_3 \cdot H^+ \\ OH^- \end{matrix} + C_2H_4 + H_2O.$$

It is evident that if this represents the true mechanism of the dehydration of ethyl alcohol by alumina, then we must likewise assume that all oxides which cause the dehydration of alcohol must be covered with a similar film of H^+ and OH^-. The difficulty in applying such a scheme comes when we consider that most of these oxides show also some dehydrogenating activity.

Langmuir[18] has shown that the tendency of a gas or vapor to be adsorbed on the surface of a solid is determined by the rate of evaporation from the surface. Further that this rate depends upon the magnitude of the forces acting between the atoms of the crystal and those of the adsorbed substance. According to him, these forces are of the same nature as those which hold solid bodies together, and we may look upon them as chemical forces. Adsorption is thus due to the unsaturated force fields at the surface of the solid. Selective and irreversible adsorption are due to primary valence forces. The weaker and less specific secondary adsorptions are due to secondary valence forces. From certain assumptions based on his own data, Benton[19] has devised a method of calculating the relative magnitudes of primary and secondary adsorption. He finds that there is no relation between the total adsorption on the surface of an adsorbent and its catalytic activity; on the other hand, the magnitude of the primary adsorptions calculated are in the same order as the catalytic activities of the substances.

In a recent paper Taylor[20] has advanced a theory of adsorption to explain the catalytic activity of solids. While he assumes with Langmuir an unbalanced force at the surface of a solid, he develops the idea of this force in a somewhat different way. According to Taylor, the atoms on a plane surface of a solid are saturated in three dimensions by neighboring atoms. There is

[16] Boswell and Bayley; J. Phys. Chem., **29**, 679 (1925).
[17] Boswell amd Dilworth: J. Phys. Chem., **29**, 1489 (1925).
[18] Langmuir: J. Am. Chem. Soc., **38**, 2267 (1916).
[19] Benton: J. Am. Chem. Soc., **45**, 887 (1923).
[20] Taylor: J. Phys. Chem., **30**, 145 (1926).

left, however, one degree of unsaturation directed toward the gaseous phase. It follows then that atoms which lie on the edge of a solid will have two degrees of unsaturation; those on a corner will have three degrees of unsaturation directed toward the gaseous phase. The attractive forces exerted by the atoms of the adsorbent upon the impinging molecules will, therefore, be greatest at the corners and least on the plane surfaces. Thus, points are considered as representing places of preferential adsorption.

That these oxides may possess an extensive capillary structure is also without question. We should expect, therefore, a wide variation in their adsorption power depending not only upon the shape, the diameter and the depth of the capillaries, but also upon the shape and volume of the adsorbed molecules. The possibility that both surface and capillary forces are active only adds to the complexity of the adsorption process.

In order to obtain some insight into the possible mechanism of ester catalysis by metallic oxides, Pearce and Alvarado[21] have measured the adsorption of water, ethyl alcohol, acetic acid and ethyl acetate vapors by thoria and alumina at 99.4°. They find that if we consider the adsorption of vapor by a unit mass of adsorbent, X/m, the results obtained show that alumina is a better adsorbent for water vapor, ethyl alcohol and ethyl acetate than is thoria. Whereas, on the basis of vapor adsorbed by 1 cc. of the oxide, X/V, thoria appears to be the better adsorbent for water vapor at all pressures, and for ethyl alcohol at low pressures. At all pressures the acetic and ethyl acetate vapors are more highly adsorbed by the aluminum oxide. If the adsorption magnitudes are calculated on the basis of equal volumes of the oxide adsorbents, the order of magnitude for the adsorption of water vapor, and for ethyl alcohol at low pressures, is the same as the order of decreasing dehydrating power of the oxides for alcohol. The magnitude of the adsorption of the vapors was found to vary with the nature of the vapor; it is greatest for water vapor and least for ethyl acetate, with alcohol occupying an intermediate position. The adsorption of acetic acid vapor seems to vary more specifically both with the nature of the oxide and with its degree of hydration.

In the present work we have continued the study of the adsorption of these vapors by the oxides of tungsten and zirconium.

Materials

Tungstic Oxide.—A large sample of the C.P. tungstic acid was dissolved in ammonium hydroxide; the solution was boiled to expel the free ammonia, and sufficient nitric acid was added to precipitate the oxide, WO_3. The precipitate was washed by decantation until the wash water showed no traces of nitrates, then filtered through hardened filter and thoroughly washed. The oxide was then dried for 24 hours at 130° and pulverized to pass through a 200-mesh sieve. After a second heating at 250° for 24 hours it was transferred to a glass-stoppered bottle and stored in a desiccator over P_2O_5.

[21] Pearce and Alvarado: J. Phys. Chem., 29, 256 (1925).

Zirconium Oxide.—The C.P. zirconium nitrate was dissolved in water and precipitated by ammonia. The subsequent treatment was the same as that used in preparing the tungstic oxide.

The method followed in purifying the solvents was the same as that employed in the previous paper.[21]

In order to determine the volume occupied by the adsorbent it was necessary to know the density of each oxide. A sample of the oxide was evacuated to less than 0.0001 mm. at 500° in a bulb provided with a drawn-out capillary. After evacuation the tube was sealed and the bulb weighed. The seal was broken under pure benzene, where it was allowed to remain for a time to allow for the drift; the level of the liquid was brought to a given mark at 25° and the bulb was again weighed. The density values obtained for the ZrO_2 were 5.489, 5.480 and 5.482, the mean being 5.484. For WO_3 the results were 6.924, 6.926 and 6.923, the mean being 6.294.

Apparatus and Manipulation

The apparatus used was similar to that used by Coolidge[22] in his study of the adsorption of vapors by charcoal. It was entirely of Pyrex, and without ground joints, stop-cocks or rubber connections. All of the parts used for measuring the gas volumes were accurately calibrated. With the exception of the vessel holding the liquid source, the whole apparatus was mounted in a large double-walled thermostat. This was electrically heated and electrically controlled at 70° ± 0.05 throughout the whole series of measurements. The temperature of the oxide bulb was kept constant by immersion in a flask containing boiling water. Hence the temperature was subject only to changes due to fluctuations in barometric pressure. The whole apparatus was evacuated by means of a Hyvac pump in series with a mercury vapor condensation pump. The vacuum obtained was read from a McLeod gauge.

In every case a sample of the oxide was weighed by removing the adsorption bulb, weighing empty, and then with the oxide present.. After the bulb was replaced, the oxide was evacuated at 500° and the evacuation was continued until the gauge indicated a pressure of less than 0.00005 mm. The apparatus was then sealed and allowed to stand for 24 hours. If no appreciable pressure developed, the experiment was begun. The exact weight of the dry oxide was determined by subjecting a sample of equal weight to exactly the same heat treatment. All volumes were corrected for dead space, and were reduced to 0°, latitude 45° and sea level.

Results

Since adsorption is a surface phenomenon, it is quite obvious that for a given uniform solid adsorbent, the total magnitude of the unsaturated surface forces, as well as the capillary effects, will be directly proportional to the extent of surface. If it were possible for two different adsorbents to possess identically the same number of unsaturated surface forces per unit area of

[22] Coolidge: J. Am. Chem. Soc., **46**, 596 (1924).

surface, the two adsorbents could approximate equal adsorption capacities, per gram of solid adsorbent, only when they expose equal surfaces. Or, on the other hand, if the surface topographies of the oxides were in every way identical, we might consider the adsorption of a given gas or vapor as a measure of the relative magnitudes of these unbalanced surface forces. It is evident that all such assumptions as these are entirely out of the question when we consider the oxides used in this paper. The densities of the oxides used thus far were Al_2O_3, 2.86; ZrO_2, 5.48; ThO_2, 6.82; WO_3, 6.92. The corresponding specific volumes of the gas-free oxides were 0.349, 0.182, 0.147 and 0.145 cc. respectively. The adsorbents were all prepared in the same

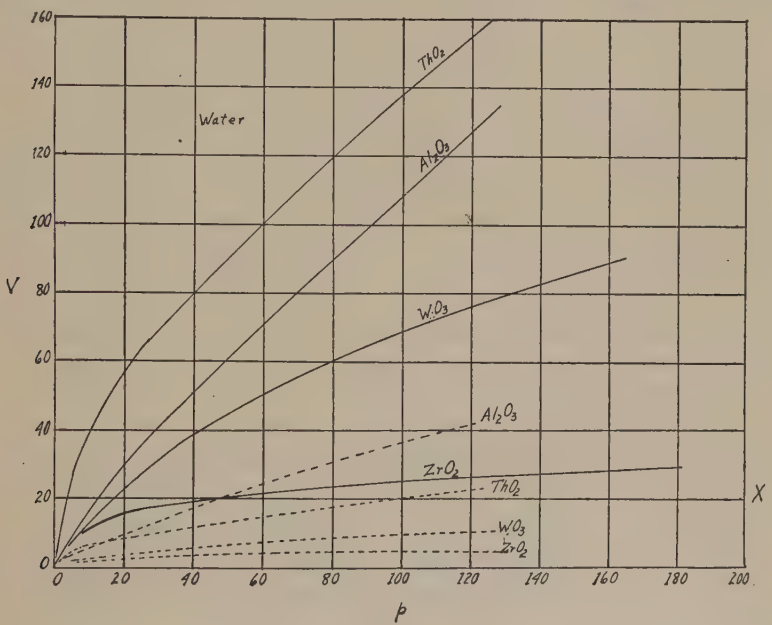

FIG. 1

V ——————
X .....

general way; in the final step all were pulverized to pass through the same mesh sieve. Assuming that the oxide particles are round and that they have the same diameter and surface topography, which is undoubtedly not true, the surface exposed by one cc. of the various oxides should be approximately the same. The surface exposed by one gram of the oxides should, on the other hand, decrease rapidly in the order of increasing density. In the study of the adsorption of gases and vapors by solid adsorbents it has been the custom, generally, to consider the volume of vapor in cc. (N.T.P.) adsorbed by 1 g. of adsorbent. For the reasons given above we believe that adsorption relations are much better expressed when the magnitudes are expressed in volumes of vapor adsorbed by 1 cc. of the solid oxide.

At least two independent series of adsorption data were obtained for each vapor on each oxide. The pressure-concentration data obtained were

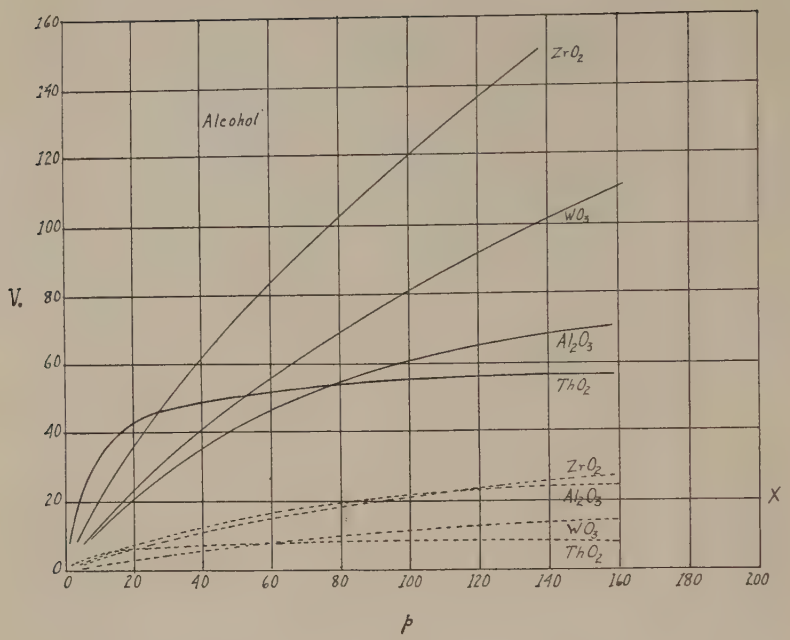
Alcohol
ZrO_2
WO_3
Al_2O_3
ThO_2
V.
X
p

FIG. 2

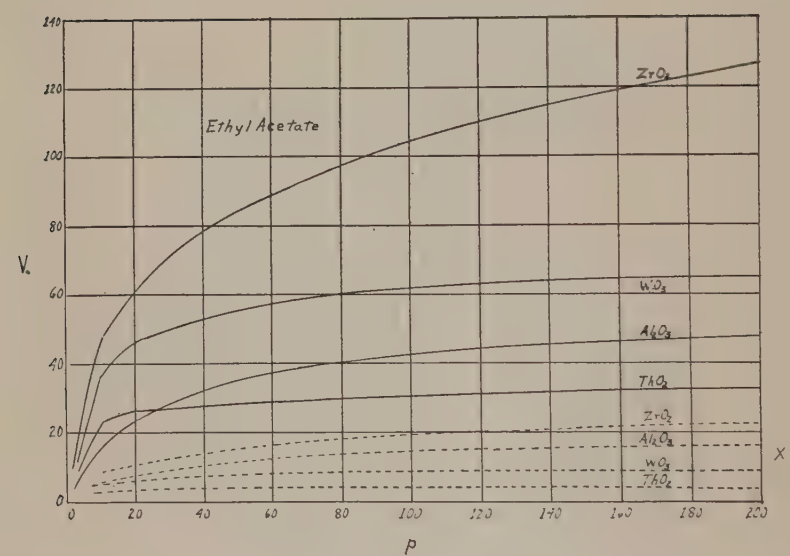
Ethyl Acetate
ZrO_2
WO_3
Al_2O_3
ThO_2
V.
X
p

FIG. 3

V ——
X .....

plotted on a large scale and a smooth isotherm was drawn through each set of points.

In the discussion which follows, X and V represent the volume of vapor in cc. (N.T.P.) adsorbed by 1 g. and by 1 cc. of the oxide, respectively. The relative adsorptive powers of ZrO_2 and WO_3 for the four vapors are clearly indicated in Figs. 1 to 4; the corresponding isotherms for the same vapors with ThO_2 and Al_2O_3[21] are included for comparison. In considering adsorption as a possible explanation of heterogeneous catalysis, we are for the present more particularly interested in the relative adsorption of each of the four vapors by each of the four different oxides. These relations are best shown in Figs. 5 to 8.

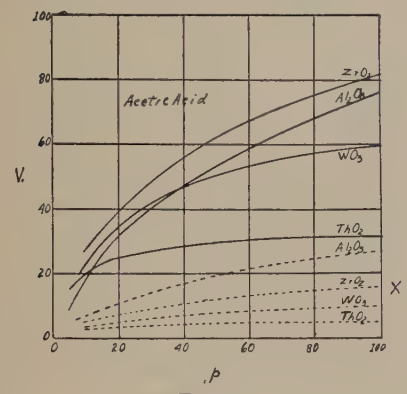

FIG. 4

V ———

X .....

Considering the volume of vapor adsorbed by 1 cc. of oxide, Fig. 1, ThO_2 has the greatest adsorption capacity for water vapor, and this capacity decreases in the order, ThO_2, Al_2O_3, WO_3, ZrO_2. Except for WO_3, this is exactly the order of the dehydrating power of these oxides toward alcohol.[11] While we have used the oxide WO_3 it falls into the same relative position below Al_2O_3 as that given by Sabatier and Mailhe for W_2O_3. The adsorption power of the first three oxides for water vapor increases rapidly with the pressure; that of ZrO_2 increases very slowly for pressures above 30 mm. When considered on the basis of cc. of vapor adsorbed by 1 gram of oxide, X, the same order obtains only for pressures below 15 mm. Above this pressure the adsorptive power of ThO_2 falls below that of Al_2O_3.

Up to about 25 mm. ThO_2 shows the greatest adsorption capacity for ethyl alcohol vapor per 1 cc. of oxide, Fig. 2. The order of decreasing capacity being ThO_2, ZrO_2, WO_3, Al_2O_3. For pressures above 75 mm. the adsorptive capacity of ThO_2 falls below that of Al_2O_3. Above 75 mm. the order of decreasing adsorption is ZrO_2, WO_3, Al_2O_3. This is exactly the reverse of the order of the dehydrating effect of these oxides on ethyl alcohol.

Except for pressures below about 25 mm., Fig. 3, where the adsorption capacity of ThO_2 is greater than that of Al_2O_3, the adsorption of ethyl acetate vapor by 1 cc. of oxide decreases in the order, ZrO_2, WO_3, Al_2O_3, ThO_2. The order is exactly the same as that observed for alcohol vapor at high pressures, and is exactly the reverse of that of the dehydrating power of the oxides.

For pressures less than 10 mm., Fig. 4, the adsorption of acetic acid vapor in decreasing order is ZrO_2, WO_3, ThO_2, Al_2O_3. At about this pressure the adsorptive capacity of Al_2O_3 begins to exceed that of ThO_2; at about 37 mm. it rises above that of WO_3. On the basis of 1 gram of oxide Al_2O_3 is at all pressures the best adsorbent for acetic acid vapor. This is then followed

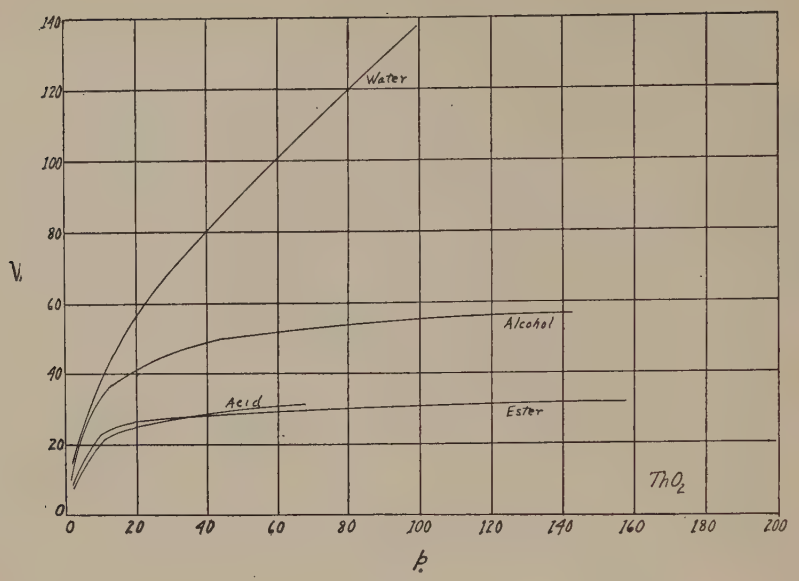

FIG. 5
Adsorption of Vapors on ThO_2

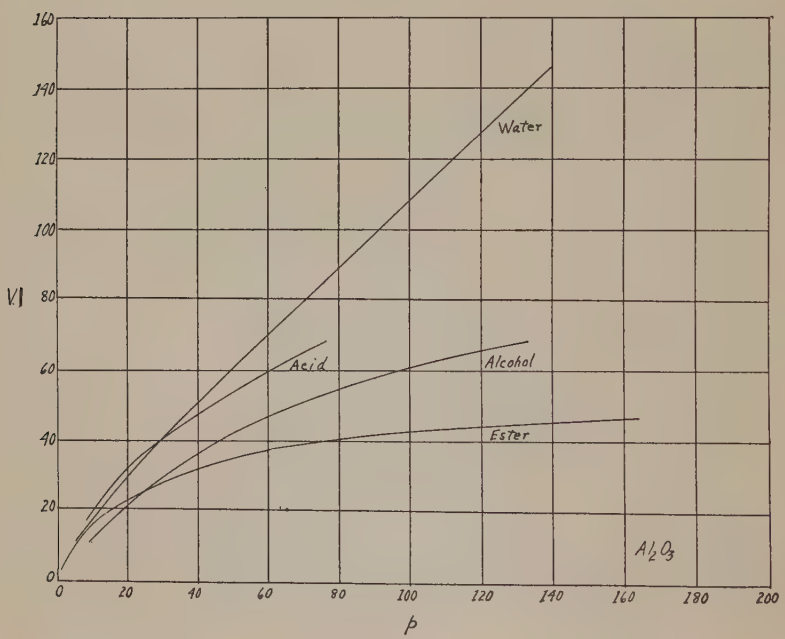

FIG. 6
Adsorption of Vapors on Al_2O_3

by ZrO_2, WO_3 and ThO_2 in the order named. The pronounced acid property of the acetic acid may exert a more or less specific influence, depending on the nature of the adsorbing oxide.

The relations shown in Figs. 5 to 8 appear to show definitely that in the heterogeneous esterification process the adsorption of one or both of the reactants, and possibly of one of the products,—the ester, may be involved. At low pressures the ester and acetic acid vapors are more highly adsorbed by WO_3 and ZrO_2 than are water vapor and alcohol. With both of these oxides, however, the amount of alcohol adsorbed by 1 cc. of oxide increases rapidly with the pressure.

At a given temperature and pressure each oxide will possess a characteristic specific adsorption for each of the four vapors. Unless a vapor is irreversibly adsorbed it may, according to the Mass Law, be displaced by increasing the concentration, or the partial pressure of a second vapor. The relative displacing powers of the different vapors on a given oxide at a given pressure are to a considerable degree at least indicated by the P-V isotherms of Figs. 5 to 8. Unless the surface of an oxide possesses different types of elementary spaces, each type capable of adsorbing molecules of one vapor to the exclusion of molecules of the other three, the water vapor will be most preferentially adsorbed by ThO_2 and to a slightly less extent by Al_2O_3. Since the alcohol at the same pressure is also highly adsorbed, the presence of both the alcohol and water vapors would practically exclude the simultaneous adsorption of acetic acid vapor, and therewith one of the essential reactants of the esterification process. Indeed, if the pressure of the water vapor is so large that the rate of evaporation is less than the rate of condensation, then it is possible for the surface of the catalyst to become so covered with water molecules that even the alcohol would no longer be adsorbed. If such were the case, the dehydration of the alcohol by these oxides would be at most only minimal in quantity. This statement is borne out by the work of Engelder. He found that by increasing the proportion of water vapor in the alcohol passed over TiO_2 the dehydration of alcohol to ethylene is decreased to a marked degree.

In their previous paper, Pearce and Alvarado[21] were inclined to favor the view that in the dehydration of alcohol by ThO_2 and Al_2O_3, the initial step in the process is the formation of the highly adsorbed water vapor and ethylidene. The ethylidene then rearranges to form ethylene. We have found nothing since that would lead us to modify that view. Both ThO_2 and Al_2O_3 are dominantly dehydrating catalysts; they exhibit but little tendency to catalyze the esterification of the aliphatic acids and alcohols.

Nothing has been observed in the literature relative to the esterifying property of ZrO_2. It lies just below TiO_2 in the list of Sabatier and Mailhe. They have found that TiO_2 rapidly catalyzes the esterification process at 280° to 300° with the production of high concentrations of the ester. Whether or not TiO_2 is the best oxide catalyst for this reaction is still a question. With rise in temperature the adsorption of the four vapors by any oxide will de-

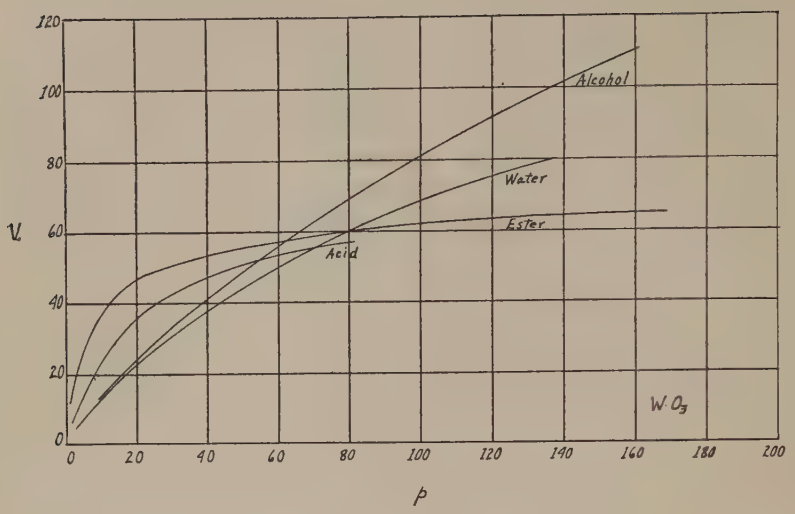

FIG. 7
Adsorption of Vapors on W_2O_8

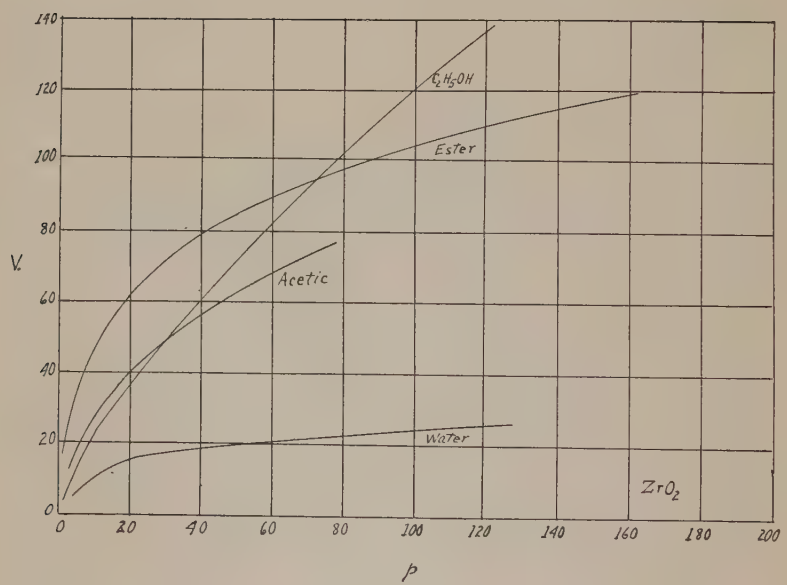

FIG. 8
Adsorption of Vapors on ZrO_2

crease, and obviously at different rates. The amount of each vapor adsorbed under a given pressure at the optimum temperature, say 280°, will be less than at the temperature at which we have made our experiments. The adsorption capacity of ZrO_2 for water vapor should be relatively very much less than its capacity for adsorbing acetic acid and alcohol. The inhibiting power of the water vapor is thus decreased and the reaction proceeds with greater velocity. On the basis of these considerations we may not be far amiss in assuming that the esterifying power of ZrO_2 is of the same order as, or possibly greater than, that of TiO_2.

If we may be allowed to speculate as to the mechanism of esterification, using such catalysts as TiO_2 and ZrO_2, it would seem from the results shown that the initial step consists in the adsorption of both alcohol and acetic acid vapors. Under the conditions of temperature and pressure a stress is produced which weakens the primary valences of the molecules, and metathesis ensues with the formation of the ester and the water vapor. The less strongly adsorbed water is vaporized and the ester is displaced by the adsorption of more acid and alcohol.

Summary

1. The adsorption of water, ethyl alcohol, acetic acid and ethyl acetate vapors by tungsten and zirconium oxides has been studied at 99.4°. The results obtained have been compared with those of a similar study of the adsorption of the same vapors by thoria and alumina.

2. For unit volume of adsorbent the adsorption capacities for water vapor decreases in the order ThO_2, Al_2O_3, WO_3, ZrO_2. This is also the order also of the dehydrating power of these oxides toward alcohol. The order of adsorption for ethyl acetate is exactly the reverse of that for water vapor.

3. The results confirm the view that in the catalytic process both the alcohol and acetic acid vapors must be adsorbed simultaneously. Further, that the catalytic effect increases as the power of the oxide to adsorb water decreases.

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BIOGRAPHY

Murray John Rice was born July 11, 1898 at Flint, Michigan. His undergraduate work was taken at Kalamazoo College, where he received the B.S. degree in 1919. One year of graduate work was taken at Clark University, and the A.M. degree was granted in 1920. During the next four years he was engaged in chemical work for the Buick Motor Co., and as a teacher in Flint Central High School and Georgetown College. He entered the State University of Iowa in June 1924 and held a fellowship for the following year. During the past year he has been a graduate assistant in chemistry.